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(54) **A process for preparing monomers**

(57) A process for preparing monomers useful in a wide range of polymers is disclosed.

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anoate, cupric fluoride, cupric gluconate, cupric nitrate, cupric methoxide, cupric sulfate, and cupric dibutyl dithio carbamate. Cupric dibutyl dithio carbamate is preferred. Suitable nitroxyl radical containing compounds include 2,2,6,6-tetramethyl-1-piperidinyloxy, free radical ("4-hydroxy-TEMPO"), 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy, free radical ("4-oxo-TEMPO"), and di-tertiary butyl nitroxyl (DTBN)(available through Nova Molecular Technologies, Lake Geneva, Wisconsin). The inhibitor may be added at from 100 ppm to 4,000 ppm based on the total weight of the synthetic wax alcohol and (meth)acrylate ester to be reacted. More preferred is from 500 ppm to 3,000 ppm inhibitor based on the total weight of the synthetic wax alcohol and (meth)acrylate ester to be reacted. Most preferred is from 1,000 ppm to 2,000 ppm inhibitor based on the total weight of the synthetic wax alcohol and (meth)acrylate ester to be reacted.

The following examples are intended to illustrate the process for making synthetic wax monomers from synthetic wax alcohols. All percentages are on a weight basis. Abbreviations used are: g = grams, mm = millimeters, l = liter, % = percent, N₂ = nitrogen, O₂ = oxygen, n = normal, and °C = degrees Centigrade.

Example 1 - Acrylate Of C₄₀ Alcohol

A 5 l flask equipped with an overhead stirrer, a 10 plate - 2 inch Oldershaw column, a thermocouple and controller, a graduated receiver, a magnetically controlled reflux head, and an 8% O₂ / 92% N₂ sparge at 19.5 cubic centimeters per minute was charged with 2,000 g of Unilin™ 550 (a primary, linear synthetic wax alcohol). To this was added 1,164 g n-butyl acrylate and 1.4 g 4-hydroxy-TEMPO. While agitating and sparging, the batch was heated to 100°C. When a homogenous solution was obtained, 20.0 g zirconium acetylacetonate was added. The vacuum was increased to 200 mm and the temperature was increased to 120°C - 125°C. The vacuum and temperature were held constant until the vapor temperature reached 97°C. At this point, transesterification was complete. The total time from zirconium acetyl acetate addition to completion of the reaction was 2.45 hours. The vacuum and temperature were lowered. The column was removed and a straight-lead take-off head was installed. The vacuum was then increased to 25 mm and the temperature was increased to 125°C. The temperature and vacuum were held until distillation stopped. The molten product was dropped out at 125°C. Conversion of the Unilin™ 550 alcohol to the acrylate ester was quantitative as measured by Nuclear Magnetic Resonance ("NMR"). The product contained 0.12% residual butyl acrylate as measured by Gas Chromatography ("GC").

Example 2 - Acrylate Of C₅₀ Alcohol

A 5 l flask equipped with an overhead stirrer, a 10

plate - 2 inch Oldershaw column, a thermocouple and controller, a graduated receiver, a magnetically controlled reflux head, and an 8% O₂ / 92% N₂ sparge at 19.5 cubic centimeters per minute was charged with 2,500 g of Unilin™ 700 (a primary, linear synthetic wax alcohol). To this was added 1,250 g n-butyl acrylate and 1.75 g 4-hydroxy-TEMPO. While agitating and sparging, the batch was heated to 100°C. When a homogenous solution was obtained, 25.0 g zirconium acetylacetonate was added. The vacuum was increased to 200 mm and the temperature was increased to 120°C - 125°C. The vacuum and temperature were held constant until the vapor temperature reached 97°C. At this point, transesterification was complete. The total time from zirconium acetyl acetate addition to completion of the reaction was 2.37 hours. The vacuum and temperature were lowered. The column was removed and a straight-lead take-off head was installed. The vacuum was then increased to 25 mm and the temperature was increased to 125°C. The temperature and vacuum were held until distillation stopped. The molten product was dropped out at 125°C. Conversion of the Unilin™ 700 alcohol to the acrylate ester was 98.5% as measured by NMR. The product contained 0.1% residual butyl acrylate as measured by GC.

Example 3 - Acrylate Of C₂₂ Alcohol

A 5 l flask equipped with an overhead stirrer, a 10 plate - 2 inch Oldershaw column, a thermocouple and controller, a graduated receiver, a magnetically controlled reflux head, and an 8% O₂ / 92% N₂ sparge at 19.5 cubic centimeters per minute was charged with 456.4 g of Nafol™ 1822 Alcohol (a primary, linear synthetic wax alcohol/100% functionality). To this was added 581.5 g n-butyl acrylate and 0.7 g 4-hydroxy-TEMPO. While agitating and sparging, the batch was heated to 100°C. When a homogenous solution was obtained, 9.9 g zirconium acetylacetonate was added. The vacuum was increased to 200 mm and the temperature was increased to 120°C - 125°C. The vacuum and temperature were held constant until the vapor temperature reached 97°C. At this point, transesterification was complete. The total time from zirconium acetyl acetate addition to completion of the reaction was 0.90 hours. The vacuum and temperature were lowered. The column was removed and a straight-lead take-off head was installed. The vacuum was then increased to 25 mm and the temperature was increased to 125°C. The temperature and vacuum were held until distillation stopped. The molten product was dropped out at 125°C. Conversion of the Nafol™ 1822 Alcohol to the acrylate ester was quantitative as measured by NMR. The product contained 0.24% residual butyl acrylate and 0.08% residual butanol as measured by GC.

ual methyl methacrylate as measured by GC.

Example 8 - Methacrylate Of Ethoxylated Alcohol With Hydroquinone Inhibitor

A 5 l flask equipped with an overhead stirrer, a 10 plate - 2 inch Oldershaw column, a thermocouple and controller, a graduated receiver, a magnetically controlled reflux head, and an 8% O₂ / 92% N₂ sparge at 19.5 cubic centimeters per minute was charged with 451 g of Unithox™ 450 (an ethoxylated primary, linear synthetic wax alcohol/82% functionality). To this was added 719 g methyl methacrylate and 1.0 g hydroquinone. While agitating and sparging, the batch was heated to 100°C. When a homogenous solution was obtained, 3.77 g zirconium acetylacetonate was added. The vacuum was increased to 200 mm and the temperature was increased to 108°C. The reaction was distilled for 2.5 hours. The total time from zirconium acetyl acetate addition to completion of the reaction was 3.0 hours. The vacuum and temperature were lowered. The column was removed and a straight-lead take-off head was installed. The residual methyl methacrylate was stripped for another 1 hour. The molten product was dropped out at 108°C. Conversion of the Unithox™ 450 alcohol to the methacrylate ester was 92% as measured by NMR. The product contained 0.44% residual methyl methacrylate as measured by GC.

Example 9 - Comparative Example - Acrylate Of C₄₀ Alcohol With Potassium tert-Butoxide

A 5 l flask equipped with an overhead stirrer, a 10 plate - 2 inch Oldershaw column, a thermocouple and controller, a graduated receiver, a magnetically controlled reflux head, and an 8% O₂ / 92% N₂ sparge at 19.5 cubic centimeters per minute was charged with 2,000 g of Unilin™ 550 (a primary, linear synthetic wax alcohol). To this was added 1,164 g n-butyl acrylate and 1.4 g 4-hydroxy-TEMPO. While agitating and sparging, the batch was heated to 100°C. When a homogenous solution was obtained, 20.0 g potassium tertbutoxide was added. The vacuum was increased to 200 mm and the temperature was increased to 120°C - 125°C. The vacuum and temperature were held constant until the vapor temperature reached 97°C. The total time from zirconium acetyl acetate addition to completion of the reaction was 2.45 hours. The vacuum and temperature were lowered. The column was removed and a straight-lead take-off head was installed. The vacuum was then increased to 25 mm and the temperature was increased to 125°C. The temperature and vacuum were held until distillation stopped. The molten product was dropped out at 125°C. Conversion of the Unilin™ 550 alcohol to the acrylate ester was 10.7% as measured by NMR. The product contained 0.63% residual butyl acrylate as measured by GC.

Example 10 - Comparative Example - Acrylate Of C₄₀ Alcohol With Dibutyltin Methoxide

A 5 l flask equipped with an overhead stirrer, a 10 plate - 2 inch Oldershaw column, a thermocouple and controller, a graduated receiver, a magnetically controlled reflux head, and an 8% O₂ / 92% N₂ sparge at 19.5 cubic centimeters per minute was charged with 2,000 g of Unilin™ 550 (a primary, linear synthetic wax alcohol). To this was added 1,164 g n-butyl acrylate and 1.4 g 4-hydroxy-TEMPO. While agitating and sparging, the batch was heated to 100°C. When a homogenous solution was obtained, 20.0 g dibutyltin dimethoxide was added. The vacuum was increased to 200 mm and the temperature was increased to 120°C - 125°C. The vacuum and temperature were held constant until the vapor temperature reached 97°C. At this point, transesterification was complete. The total time from zirconium acetyl acetate addition to completion of the reaction was 2.45 hours. The vacuum and temperature were lowered. The column was removed and a straight-lead take-off head was installed. The vacuum was then increased to 25 mm and the temperature was increased to 125°C. The temperature and vacuum were held until distillation stopped. The molten product was dropped out at 125°C. Conversion of the Unilin™ 550 alcohol to the acrylate ester was quantitative as measured by NMR. The product contained 0.64% residual butyl acrylate as measured by GC. Although the conversion was good, tin is quite toxic and has to be removed from the product. Removal of tin from the product is very difficult.

Example 11 - Comparative Example - Acrylate Of C₄₀ Alcohol With Magnesium Methoxide

A 5 l flask equipped with an overhead stirrer, a 10 plate - 2 inch Oldershaw column, a thermocouple and controller, a graduated receiver, a magnetically controlled reflux head, and an 8% O₂ / 92% N₂ sparge at 19.5 cubic centimeters per minute was charged with 2,000 g of Unilin™ 550 (a primary, linear synthetic wax alcohol). To this was added 1,164 g n-butyl acrylate and 1.4 g 4-hydroxy-TEMPO. While agitating and sparging, the batch was heated to 100°C. When a homogenous solution was obtained, 20.0 g magnesium methyl carbonate (8% in methanol) was added. The vacuum was increased to 200 mm and the temperature was increased to 120°C - 125°C. The vacuum and temperature were held constant until the vapor temperature reached 97°C. The total time from zirconium acetyl acetate addition to completion of the reaction was 2.45 hours. The vacuum and temperature were lowered. The column was removed and a straight-lead take-off head was installed. The vacuum was then increased to 25 mm and the temperature was increased to 125°C. The temperature and vacuum were held until distillation stopped. The molten product was dropped out at 125°C. Conversion of the Unilin™ 550 alcohol to the acrylate ester was 1.5% as



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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 7768

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.8)
Y	FR 2 602 229 A (SOCIETE CHIMIQUE DES CHARBONNAGES S.A.) * page 1, line 17 - page 2, line 14 * * page 3 - page 4; example 1 * * page 6 - page 7; claims *	1-3,5,6	C07C67/03 C07C69/54
Y	DE 28 05 702 A (MITSUBISHI RAYON CO.LTD.) * page 1 - page 3; claims * * page 6, line 1 - page 8, line 13 * * page 8, line 21 - line 27 * * page 10 - page 11; examples 1,5 *	1-3,5,6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C07C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 January 1998	Examiner Kinzinger, J
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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